

Article

Characterization and Analysis of Volatile Fingerprint of 13 Different Commercial Essential Oils with GC-MS and Chemical Gas Sensors

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Abstract: Essential oils are mixtures of compounds obtained from plants, including flowers, roots, bark, leaves, seeds, peel, fruits, wood, that have risen up in the last decades thanks to their beneficial properties as antibacterial, antifungal and anti-inflammatory agents. The aim of this study was to characterize and analyze 13 different commercial essential oils with two different techniques. The first is GC-MS, coupled with SPME, thanks to which 204 different VOCs have been identified. The results show that a total of 95 compounds was found only in one oil, while the others were found with different frequencies in many of them. The most represented class is that of terpenes, as widely reported in literature. The second technique is based on an array of chemical gas sensors. This system was used to investigate whether sensors are able to identify these products. It turned out that basil, cinnamon and carnation are the most identifiable oils with different number and typology of sensors, especially tin oxide and copper oxide nanowires, while cayeput and thyme are more mistakable samples. Thanks to this detailed study, it has been possible to reach and obtain novel insights for the future development of this type of research.

Keywords: essential oils; VOCs; GC-MS SPME; electronic nose; nanowire gas sensors; ANOVA.

1. Introduction

Essential oils (EOs) are complex mixtures of compounds extracted as secondary metabolites from aromatic plants. Since they are hydrophobic and have often a density lower than that of water, are lipophilic and soluble in organic solvents [1]. EOs can be obtained in different ways, that can be grouped together in two main classes: classical methods, such as hydro distillation [2] and cold pressing [3], and innovative techniques, as supercritical fluid extraction [4,5]. The extraction is regulated by International Standards Organization (ISO) [6].

EOs were well known since ancient civilizations, such as the Egyptians and the Persians, for their antiseptic, fungicidal and antimicrobial properties, that have been preserved until today [7]. All these characteristics are back to be investigated in recent years as they give the EOs the potential to be used in many fields. Food preservation is one and green materials are gaining attention for the development of biodegradable packaging materials. Hence, the incorporation of EOs in new films brings two advantages, *i.e.* antimicrobial activity and physicochemical properties improvement [8–13]. Related to this field, EOs are promising substances as antibiotic alternatives in animal production

like poultry and swine, although the metabolisms and the mechanisms of their activities should be better understood [14–16]. In the last years, several studies have been carried out in order to understand the antimicrobial effects of different oils on microorganisms and foodborne pathogens [17]. As examples, the effects of cardamom, cumin, and dill weed EOs have been investigated against *Campylobacter spp.* [18]; basil, oregano and thyme were effective against *E. coli*, *Salmonella enteritidis*, *L. monocytogenes* [19,20]; oils extracted from dill herb (leaves and seed) were used for their antifungal and antimicrobial capability towards *Aspergillus* genus and *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, respectively [21]; coriander has shown the higher antimicrobial activity among ten Apiaceous fruit against *E. coli* and *Bordetella bronchiseptica* [22]; six different juniper species were examined to evaluate which were the effects on different bacteria [23].

Finally, among all the benefits of EOs, it is important to remember also their medicinal and therapeutic potentials. They are antioxidant and anti-aging [24], cancer preventive and anti-inflammatory [25].

On the other hand, in the last years a high interest has risen up regarding the use of chemical sensors to perform rapid and cost-efficient analysis in many different fields of application. The main fields of application for this kind of technology are environmental [26–29] and health monitoring [30–31], followed up by quality control in foods [32–33]. Nowadays a lot of different types of chemical sensor are on the market, one of the most used categories are Metal Oxide (MOX) sensors that bases their working principle in the semiconductor characteristics of these materials. Nanowire MOX gas sensor (NWs) [34] are one of the many different semiconductor chemical sensors but in particular this kind of technology merge also the main characteristics of the nanostructured materials, as high length to width ratio, which reduce the threshold of detection of some compounds, and long-term stability for sustained operation. The promising performances NWs have been extensively reported in literature in many different fields as environmental and health monitoring [35–37] and food quality control [38–40].

The aim of this work was to characterize and analyze the set of volatile organic compounds (VOCs) of thirteen different commercial EOs. The study proceeded in two steps. First of all, a Gas Chromatograph with Mass Spectrometer (GC-MS) has been used in order to identify the compounds of the samples and to understand which were common and which distinctive of the specific sample. This technique is widely used for this purpose [41,42]. GC-MS has been coupled with Solid Phase Micro Extraction (SPME) technique. Secondly, an analysis with array of nanowire gas sensors placed in an innovative device called Small Sensor System (S3) was carried out.

2. Results & Discussion

2.1. GC-MS Analysis

GC-MS analysis, of the 13 EOs samples, led to the identification of 204 different VOCs. In Table 1, they are reported for increasing retention time (Rt), starting from 2.04 min to 58.61 min. The samples to which the compounds belong and the abundance are indicated. Abundance has been calculated as the mean value of the two replicas of the peak areas obtained from the chromatogram, every samples was analyzed in two replicas. Values are scaled by a factor of 10^{-6} . The name of most compounds has been found mainly in two References [43–44].

Table 1. List of VOCs found in the 13 EOs with retention time (Rt) and pick areas. Abundance of the area is the mean of two replicas. Values are scaled by a factor of 10^{-6} . B=basil, Ci=cinnamon, Card=cardamom, Cay=cayeput, Co=coriander, Carn=carnation, J=Jupiter, Ni=niaouly, Nu=nutmeg, O=oregan, R=rosemary, M=mustard, T=thyme.

Rt	VOCs	Area
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		<i>B</i>	<i>Ci</i>	<i>Card</i>	<i>Cay</i>	<i>Co</i>	<i>Carn</i>	<i>J</i>	<i>Ni</i>	<i>Nu</i>	<i>O</i>	<i>R</i>	<i>M</i>	<i>T</i>
2.04	N,N-Dimethyl-3-Buten-1-amine	0	0	0	0	0,266	0	0	0	0	0	0	0	0
2.08	Methoxyethylene	0	0	4,002	0	0	0	0	0	0	0	0	0	0
2.70	Cyclopropylamine	0	0	0	0	0	0	0	0	0	0	0	68,866	0
4.51	1R- α -Pinene	0	246,652	209,99	120,922	688,009	0	2395,5 15	127,54	973,149	229,777	1353,925	0	492,95 5
5.14	(2-Methyloctyl)benzene	0	0	0	0	0	3,955	0	0	0	0	0	0	0
5.15	2-Methyl-2-(2,2,4,4-tetramethylpentyl)-aziridine	0	0	0	0	0	0	0	0	0	0	0	0,477	0
5.57	Camphene	0	79,731	0	28,776	153,889	0	0	28,37	0	59,521	697,084	0	183,77 4
7.21	β -Pinene	0	71,616	31,439	154,377	48,345	0	128,50 3	161,683	573,457	336,578	1088,569	0	52,663
8.14	β -Phellandrene	0	28,348	625,935	0	0	0	163,95 4	0	135,488	0	0	0	0
8.37	3-Isopropenyl-5,5-dimethyl-cyclopentene	0	0	0	0	0	0	0	0	1688,54 8	0	0	0	0
8.54	1-Methoxy-2-propanol	0	8,844	0	19,662	8,435	8,021	0	17,313	0	13,46	0	5,133	0
8.66	1-(1-Methoxymethoxyethyl)cyclohexane	0	0	0	0	0	0	0	0	0	0	0	0	23,654
9.54	Diallyl sulfide	0	0	0	0	0	0	0	0	0	0	0	156,129	0
9.91	3-Heptanone	5,741	0	6,038	10,318	9,88	19,626	0	10,655	0	0	0	0	7,372
10.2 3	α -Phellandrene	0	253,238	0	0	0	0	0	0	71,01	0	0	0	0
10.6 3	β -Myrcene	0	0	84,547	62,101	26,488	0	714,58 1	65,17	0	477,578	0	0	230,67 1
11.4 2	α -Ethylcaproaldehyde	1,574	0	0	0	0	1,227	0	0	0	0	0	3,096	0
11.8 8	D-Limonene	0	82,25	0	0	412,02	0	2041,2 69	0	0	0	0	0	301,65 5
11.9 7	1,4-Dimethyl-4-vinylcyclohexene	0	0	0	0	0	0	0	0	419,344	0	0	0	0
12.0 5	β -Terpineol	0	0	0	0	0	0	0	0	0	156,956	0	0	0
12.1 2	Eucalyptol	296,274	184,082	2006,264	2884,90 4	0	0	0	2977,09	309,084	0	2826,559	0	0
12.3 6	Methoxybutanol	0	0	0	0	0	8,397	0	0	0	0	0	7,902	0
12.9 0	Thiazole	0	0	0	0	0	0	0	0	0	0	0	30,169	0
13.3 0	1-[1-Cycloazapropyl]-n-Octane	8,728	6,491	0	0	8,113	6,295	7,071	0	14,781	8,788	0	0	0
13.4 3	8-Methylenepentadecane	0	0	0	39,637	0	0	0	46,818	0	0	36,451	0	0
13.7 1	1-Decylaziridine	0	0	0	0	0	0	0	0	0	0	0	0	6,153
14.1 3	γ -Terpinene	0	48,044	0	25,79	82,952	0	63,32	27,452	463,12	559,739	137,353	0	0
14.3 9	1-Undecene	0	0	0	0	0	1,007	0	0	0	0	0	0	0
14.7 3	N-[(4-Hydroxy)hydrocinnamoyl]-Benzeneethanamine	0	24,029	0	0	0	0	0	0	0	0	0	0	0
14.8 2	β -Ocimene	0	0	0	44,073	0	0	0	47,878	0	0	29,047	0	0
15.0 8	1-Butoxy-2-ethylhexane	0	0	0	0	0	0	0	0	0	0	0	2,564	0
15.1 9	p-Cymene	8,272	0	0	0	0	12,989	0	0	0	0	0	0	0
15.2 7	m-Cymene	0	339,522	93,37	63,366	0	0	91,267	66,913	216,747	0	333,558	0	0
15.3 8	o-Cymene	0	0	0	0	584,098	0	0	0	0	1201,20 3	0	0	2115,9 68
15.7 1	(+)-4-Carene	0	7,473	0	18,686	5,163	0	235,03 4	0	868,631	180,754	194,837	0	0

15.85	1-Azepan-1-yl-2-bromethanone	0	0	0	0	0	0	0	0	0	0	0	9,566	0
15.88	Lactic acid, monoanhydride with 1-butaneboronic acid, cyclic ester	76,743	37,209	120,834	103,031	85,449	84,357	0	130,325	0	0	0	61,796	0
16.87	Tridecane	0	21,214	0	0	0	32,486	0	0	2,202	0	0	0	0
17.59	3-Butyl-cyclohexanone	0	0	0	0	0	0	0	0	0	0	0	12,456	0
17.83	2-Heptanol	0	0	0	0	0	5,36	0	0	0	0	0	0	0
17.99	1-Adamantanol	0	0	0	0	0	0	0	0	2,739	0	0	0	0
18.31	Methyl Heptenone	0	0	44,593	0	0	0	0	0	0	0	0	0	0
18.41	Nonanenitrile	22,089	17,107	0	25,576	25,716	30,884	18,898	26,007	14,007	18,511	29,649	18,683	14,803
19.08	Hexyl formate	74,396	107,316	127,484	104,903	95,14	119,112	93,84	109,322	96,787	103,847	117,823	109,848	103,025
19.62	Neo-allo-ocimene	0	5,482	0	0	0	0	6,401	0	0	0	3,197	0	0
20.04	Ethyl glycidyl ether	0	5,741	2,276	0	2,349	4,418	0	1,793	0	6,816	0	1,71	0
20.17	cis-p-Mentha-2,8-dien-1-ol	0	0	0	0	0	0	0	0	4,856	0	0	0	0
20.65	3-Octanol	5,021	10,176	0	0	6,694	0	0	0	4,583	3,283	0	7,011	0
20.95	Tetradecane	12,912	21,943	25,936	23,953	14,859	31,797	20,273	23,981	16,134	25,493	28,78	24,445	24,8
21.25	trans-p-mentha-1(7),8-dien-2-ol	0	0	0	0	0	0	0	0	2,068	0	0	0	0
21.43	Perillene	0	0	11,594	0	0	0	4,717	0	0	0	0	0	0
21.84	Isobutylbenzene	0	15,057	0	16,845	0	0	47,556	15,861	20,973	22,514	32,065	0	13,615
22.12	1,2-Oxolinalool	6,037	0	33,755	0	80,428	0	0	0	0	0	0	0	0
22.44	(+)-(E)-Limonene oxide	0	0	6,428	0	0	0	0	0	0	0	0	0	0
22.56	1-Tridecene	4,568	0	0	0	0	4,416	0	0	0	0	0	3,601	0
22.56	Undecyl pentafluoropropionate	0	0	0	0	0	0	0	5,438	0	0	0	0	0
22.57	1,16-Dichlorohexadecane	0	0	0	5,887	0	0	0	0	0	0	0	0	6,037
22.61	α -Cubebene	0	4,186	0	0	0	0	16,334	0	28,967	0	23,464	0	0
22.65	1-Chloroeicosane	0	9,82	0	0	0	0	0	0	0	0	0	0	0
22.68	1-Tetradecene	0	0	0	0	3,353	0	0	0	0	0	0	0	0
22.77	Bicyclo[3.2.0]hept-2-ene, exo-4-tertbutoxy-	0	0	0	0	0	0	0	0	0	15,853	0	0	0
22.98	Methyl undecyl ether	0	0	0	0	0	2,203	0	0	0	0	0	0	0
23.50	Polypropylene Glycol Methyl Ether	799,489	1599,327	1654,054	178,829	765,18	833,419	0	172,517	1520,086	1615,994	99,289	910,685	0
24.13	2-Ethylhexanol	719,286	187,687	0	1385,679	0	830,527	1398,359	1417,18	147,552	797,095	0	867,047	1505,355
24.39	Camphor	0	0	0	0	1100,23	0	0	0	0	0	2232,84	0	0
24.49	Pentadecane	0	17,365	7,446	0	0	20,603	40,721	0	15,392	0	0	20,415	0
24.51	2-Octen-1-ol, 3,7-dimethyl-, isobutyrate, (Z)-	0	0	0	0	0	0	0	0	0	25,802	0	0	0
24.83	Benzaldehyde	0	13,513	0	0	0	0	0	0	0	0	0	0	0
25.38	Methyl 2,6-dideoxy- α -D-lyxohexopyranoside	830,201	920,868	912,518	776,097	811,795	885,574	790,829	789,657	881,883	878,431	843,065	974,78	827,055

26.0 6	Linalool	64,433	148,032	0	0	1344,423	0	0	0	0	135,11	0	0	290,59 6
26.2 3	β -Curcumene	0	0	0	0	0	0	551,43 7	0	0	0	0	0	0
26.3 5	1-Octanol	197,736	232,05	674,431	186,808	0	237,314	479,07 9	333,668	211,771	230,618	275,306	242,376	249,61 2
26.6 3	Dipropylene glycol monomethyl ether	54,813	68,104	0	65,324	0	63,566	85,244	63,202	62,043	69,426	0	71,982	0
27.0 5	Caryophyllene	0	626,233	7,951	37,152	1,13	72,023	143,93 7	38,026	89,446	224,473	0	27,025	155,38 8
27.4 9	4-Carvomenthenol	23,711	39,256	44,759	35,96	5,478	4,096	0	35,202	224,368	101,313	532,642	0	9,8
27.6 1	Hexadecane	6,28	0	0	0	0	11,766	0	0	0	0	0	0	0
27.6 7	1-Chloro-Heptacosane	0	6,342	0	0	0	0	0	0	0	0	0	0	0
27.8 4	Ethylene glycol monoheptyl ether	0	29,913	0	0	0	29,709	0	0	0	0	0	0	0
27.8 6	N-[2-[p-Methoxybenzyl]amino]ethylaziridine	40,312	0	0	0	0	0	0	0	0	0	0	0	0
28.0 5	1-(4-piperidinylcarbonyl) piperidine	153,789	161,876	209,939	184,506	201,02	204,666	266,74 3	221,021	200,268	182,797	214,645	234,7	193,11 6
28.3 3	cis-p-Menth-2-en-1-ol	0	0	0	0	0	0	0	0	3,932	0	0	0	0
28.4 6	Dihydro carveol	0	0	0	0	0	0	0	0	0	0	0	0	2,741
28.4 7	trans- β -Terpineol	0	0	0	25,333	0	0	0	22,948	0	0	0	0	0
28.5 1	Aromandendrene	0	7,305	0	0	0	0	0	0	0	0	0	0	0
28.5 5	γ -Elemene	0	0	0	0	0	0	59,116	0	0	0	0	0	0
28.6 6	Humulen-(v1)	0	0	0	0	0	0	0	0	0	0	3,398	0	0
28.6 9	Menthol	0	0	0	0	0	1,365	0	0	0,968	0	0	0	0
28.8 8	5-Benzoylpentanoic acid	0	3,874	0	0	0	0	0	0	0	0	0	0	0
28.9 5	α -Terpinyl acetate	0	0	0	0	0	0	0	1,306	0	0	0	0	0
29.0 1	1-Octadecene	0	0	0	0	0	1,641	0	0	0	0	0	0	0
29.0 5	β -copaene	0	0	0	0	0	0	0	0	2,428	0	0	0	0
29.0 8	Pinocarveol	0	0	6,809	0	0	0	0	0	0	0	0	0	0
29.1 1	1-Heptadecene	0	0	0	2,04	0	0	0	0	0	0	0	0	0
29.2 4	Humulene	0	128,225	0	0	0	8,32	48,543	0	9,174	1,697	73,704	0	0
29.5 2	2-(3,4-Dibromo-4-methylcyclohexyl)propan-2-ol	0	0	0	0	0	0	0	0	0	0	0	0	42,658
29.5 4	Dipropylene glycol, butyl ether	0	15,077	23,058	0	7,918	0	0	0	13,056	12,683	0	0	0
29.5 7	Anethole	38,326	0	0	43,056	0	26,319	0	81,61	0	0	0	18,306	0
29.8 7	3,3'-Oxybis-2-butanol	0	0	0	0	5,383	0	0	0	0	0	0	0	5,289
29.8 8	3-Chloro-2-methyl-2-pentanol	0	0	12,297	0	0	0	0	0	0	0	0	0	0
29.9 8	γ -Muurolole	0	12,456	0	0	0	0	71,655	0	3,273	0	85,262	0	0
29.9 8	1-[1-Methyl-2-(2-propenyloxy)ethoxy]-2-propanol	0	0	0	19,985	6,765	25,422	0	0	27,525	17,597	0	7,386	7,917
30.0 1	Myrcenol	0	0	0	0	0	0	0	20,922	0	0	0	0	0

30.1 3	Isoledene	0	50,409	0	0	0	0	0	0	0	0	0	0	0
30.2 9	Estragole	2018,738	0	0	0	0	0	0	0	0	0	0	0	0
30.4 3	L- α -Terpineol	63,995	21,515	883,389	701,913	42,932	3,479	0	723,138	25,325	46,623	178,197	0	73,644
30.6 4	Heptadecane	0	0	0	0	0	9,116	0	0	10,016	0	0	9,96	0
30.7 7	Pseudoarsasapogenin-5,20-dien methyl ether	0	14,329	0	0	0	0	0	0	0	0	0	0	0
30.7 9	Longifolene-(V4)	0	0	0	0	0	0	52,216	0	0	0	0	0	0
30.9 6	γ -Neoclovene	0	0	46,115	0	0	0	0	0	0	0	14,805	0	0
31.0 3	1,2-Nonadecanediol	0	0	0	0	0	1,122	0	0	0	0	0	0	0
31.1 1	Pentamethylcyclopentadiene	0	0	0	0	0	0	69,26	0	0	0	0	0	0
31.2 3	β -Bisabolene	0	0	0	0	0	0	0	0	5,54	7,697	9,478	0	0
31.2 5	2-Undecanol	0	1,232	1,184	0	0	0,805	0	0	0	0	0	0	0,115
31.3 4	γ -Elemene	0	0	0	5,714	0	0	0	5,469	0	0	0	0	0
31.4 1	3-chlorophenyl 2-methoxyethyl ester carbonic acid	0	0	0	0	0	0,646	0	0	0	0	0	0	0
31.6 0	[4.2.2]Propella-2,4,7,9-tetraene	4,882	0	0	0	0	0	0	0	0	0	0	0	0
31.7 4	Ethyl 2-(5-methyl-5- vinyltetrahydrofuran-2- yl)propan-2-yl carbonate	0	0	0	0	5,552	0	0	0	0	0	0	0	0
31.7 7	1-Azepan-1-yl-2-bromethanone	0	0	0	0	0	1,943	0	0	3,241	0	0	0	0
32.0 6	β -Cadinene	0	53,199	0	0	0	0	96,048	0	30,06	0	51,703	0	0
32.0 9	Octyl ether	0	0	35,804	14,093	11,88	17,81	0	17,125	0	12,27	0	13,899	14,442
32.5 3	Nonyl-cyclopropane	138,586	165,025	155,907	130,933	136,659	173,198	151,358	133,82	147,478	130,037	149,199	155,748	127,867
32.9 9	α -Cadinene	0	2,833	0	0	0	0	8,654	0	0	0	0	0	0
33.2 2	2-Butyloctanol	0	0	29,365	0	8,386	0	0	0	0	0	10,621	0	0
33.2 3	2-methyldecan-1-ol	57,986	80,795	15,622	79,421	26,102	76,32	6,351	74,938	60,145	44,958	28,523	31,801	6,512
33.4 1	Isopinocarveol	0	0	0	0	0	0	15,134	0	0	0	0	0	0
33.5 5	(S)-2-Methyl-1-dodecanol	0	0	0	0	0	5,483	0	46,717	5,156	0	0	0	0
33.6 0	1-Undecanol	0	0	0	0	0	0	0	5,534	0	0	0	0	0
34.0 4	Ethylene glycol monododecyl ether	0	18,094	12,665	15,443	10,189	18,65	22,399	19,812	13,57	9,756	16,331	14,55	12,93
34.1 1	trans-calamenene	0	0	0	0	0	0	20,503	0	0	0	0	0	0
34.4 6	trans-3-Caren-2-ol	0	0	6,559	0	1,213	0	0	0	0	0	0	0	0
34.8 8	Thymol	0	0	0	8,756	0	0	0	3,807	0	86,856	0	0	87,723
34.8 8	Geraniol	0	0	24,141	0	57,715	0	0	0	3,016	3,344	0	0	0
34.9 4	Tridecyl adamantane-1- carboxylate	0	1,678	0	0	0	0	0	0	0	0	0	0	0
35.3 3	E-11,13-Tetradecadien-1-ol	5,544	0	0	0	6,806	0	6,868	0	0	6,215	0	0	0
35.4 4	N-Methyl-N-(2- ethylhexyl)trifluoroacetamide	0	0	0	0	0	9,735	0	6,922	0	0	0	0	0

35.4 5	Safrole	0	248,239	0	0	0	0	0	0	99,36	0	28,938	0	0
35.4 5	1-(2,6-Dimethylmorpholin-4-yl)-2-ethyl-hexan-1-one	0	0	0	0	0	0	0	0	0	0	0	12,516	0
36.4 3	α -Calacorene	0	3,395	0	0	0	0	0	0	0	0	0	0	0
36.7 1	N-(2-Furanylmethylene)-3-methyl-1-butanamine	0	0	0	0	0	1,756	0	0	0	0	0	0	0
37.5 2	Caryophyllene oxide	0	40,715	0	0	0	0	0	0	0	124,189	0	0	29,331
37.5 5	Decyl ether	0	9,045	0	0	0	5,414	0	0	4,988	4,558	0	0	0
37.6 7	2,6-Dimethyl-3,7-octadiene-2,6-diol	0	0	25,187	0	16,676	0	0	0	0	0	0	0	0
37.6 7	1-Ethyl-2,3-dimethyl-piperidin-4-one	0	0	0	0	0	0	20,108	0	0	0	0	0	0
37.8 1	N-[4-Bromo-n-butyl]-2-piperidinone	0	0	0	0	0	0	0	0	0	17,168	0	0	0
38.0 9	1-Dodecanol	7,115	0	0	9,707	8,989	12,267	9,936	6,38	7,658	0	33,877	0	5,598
38.4 1	Limonene glycol	0	0	16,8	0	0	0	0	0	0	0	0	0	0
38.5 4	(2 α ,3 α ,5 β)-1,1,2-Trimethyl-3,5-bis(1-methylethenyl)-cyclohexane	0	0	0	0	0	0	0	0	0	0,921	0	0	0
38.8 3	Diethylene glycol hexyl ether	3,59	5,71	9,887	4,689	4,286	3,346	4,14	3,583	2,828	4,056	4,905	2,872	2,959
39.2 7	Benzenepropanoic acid, β -[(tert-butyl)dimethylsilyloxy]-, tert-butyl)dimethylsilyl ester	0	0	0	0	0	1,672	0	0	0	0	0	0	0
39.2 8	2-Allyl-1,4-dimethoxybenzene	0	4,292	0	0	0	0	0	0	13,476	0	3,852	0	0
39.3 0	P-Anisaldehyde	2,4	0	0	0	0	0	0	0	0	0	0	0	0
39.5 0	Humulene epoxide II	0	9,314	0	0	0	0,527	0	0	0	0	0	0	0
39.6 3	Isosafrol	0	0	0	0	0	0	0	0	0,962	0	0	0	0
39.9 2	Benzylidene-hexyl-amine	0	146,116	0	0	2,485	1,319	0	0	0	0,475	10,762	0	0
40.0 4	Nerolidol	0	0	28,949	0	0	0	3,096	0	0	0	0	0	0
40.8 6	Elemol	0	0	0	1,638	0	0	6,935	3,05	1,116	0	0	0	0
41.0 9	Guaiol	0	0	0	0	0	0	0	0	1,202	0	0	0	0
41.2 4	p-Menth-2-en-1,4-diol	0	0	0	0	0	0	0	0	0	0	4,999	0	0
41.5 1	Dehydroterpin Monoacetate	0	0	3,902	0	0	0	0	0	0	0	0	0	0
41.5 7	Cedrol	0	0	0	0	0	0	125,831	0	1,326	0,981	0	0	0
41.6 7	Acetocinnamone	0	2,301	0	0	0	0	0	0	0	0	0	0	0
41.6 9	p-Propylguaiaicol	0	0	0	0	0	0,193	0	0	0	0	0	0	0
41.8 3	Spathulenol	0	2,182	0	0	0	0	0	3,751	0,404	0	0	0	0
41.9 4	3-Acetoxy-4-(1-hydroxy-1-methylethyl)-1-methyl-cyclohexene	0	0	26,72	6,871	0	0	0	0	0	0	0	0	0
42.3 0	2,6-Dimethyl-1,7-octadiene-3,6-diol	0	0	3,248	0	2,705	0	0	0	0	0	0	0	0
42.5 5	Longifolene-I2	0	0	0	0	0	0	5,791	0	0	0	0	0	0
42.7 4	Cinnamyl ester acetic acid	0	25,656	0	0	0	0	0	0	0	0	0	0	0
42.7 9	4-Methyl-3-heptanol	3,354	0	4,683	4,549	3,469	1,271	0	5,57	2,697	4,791	3,549	2,748	2,838

43.06	Chavibetol	0	246,972	8,34	0	0	212,738	9,924	0	3,412	0	13,884	12,511	6,1
43.25	Myristyl alcohol	1,32	0	3,321	2,18	0	0	0	0	0	0	0	1,975	1,737
43.37	1-(Isooctyloxy)-2-methyl-2-propanol	1,659	6,09	2,954	0	0	7,028	0	0	4,578	0	2,653	2,511	0
43.44	α -Cadinol	0	0	0	0	0	0	67,701	0	0	0	0	0	0
43.48	Isomethyleugenol	0	0	0	0	0	0	0	0	1,457	0	0	0	0
43.71	Carvacrol	5,515	0	0	1,916	0	2,1	0	11,253	0,686	191,278	0	0,634	31,214
43.90	Geranylinalool	0	0	0	0	0	0	12,581	0	0	0	0	0	0
44.00	Diethylene glycol monododecyl ether	1,216	2,494	0	2,195	1,563	1,726	0	0	0	1,199	0	1,782	0
44.47	Hedycaryol	0	0	0	0	0	0	3,761	0	0	0	0	0	0
44.56	Asarone	0	0	0	0	0	0	0	0	36,598	0	0	0	0
44.96	cis-sesquisabinene hydrate	0	0	0	0	0	0	0	0	2,327	0	0	0	0
45.01	geranyl- α -terpinene	0	0	0	0	0	0	11,772	0	0	0	0	0	0
45.32	Myristicin	0	5,066	6,729	0	0	0	0	0	69,475	0,532	0	0	0
45.80	Cinnamyl alcohol	0	10,64	0	0	0	0	0	0	0	0	0	0	0
45.83	Benzylidene-hexyl-amine	0	0	0	0	0	0	0	0	0,656	0	0	0	0
45.87	6-Isopropenyl-4,8a-dimethyl-1,2,3,5,6,7,8,8a-octahydro-naphthalen-2-ol	0	0	0	0	0	0	10,839	0	0	3,595	0	0	0
45.91	Verbenol	0	0	6,171	0	0	0	0	0	0	3,081	0	0	0
45.97	bis(dimethylhydrazone)ethanedia 1	0	0	0	0	0	0	0	0	0	0	0	1,693	0
46.50	Sclarene	0	0	0	0	0	0	6,303	0	0	0	0	0	0
46.67	Hydroxy- α -terpenyl acetate	0	0	19,031	2,294	0	0	0	2,741	0	1,691	0	3,428	0
46.88	Manoyl oxide	0	0	0	0	0	0	9,54	0	0	0	0	0	0
46.95	Isoaromadendrene epoxide	0	2,038	0	0	0	0	0	1,167	0	15,137	3,242	0	0
47.16	(2S,6R)-1-Methyl-2,6-dipentylpiperidin-4-one	0	1,461	0	0	0	0	0	0	0	1,057	0	0	0
47.44	trans-Isoeugenol	0	2,544	0	0	0	2,207	0	0	0,396	0	1,169	0,896	0
48.00	α -Gurjunene	0	0	0	0	0	0	12,013	0	0	5,832	0	0	0
48.37	Terpineol	0	0,928	12,834	0	0	0,542	0	1,403	0	0	0	0	0
50.13	Cembrene	0	0	0	0	0	0	22,917	0	3,793	0	0	0	0
50.59	1,3,3-Trimethyl-6-hydroxy-2-oxabicyclo[2,2,2]octan-7-one	0	0	1,092	0	0	0	0	0	0	0	0	0	0
51.49	7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene	0	0	0	0	0	0	7,343	0	0	0	0	0	0
51.84	trans-Octahydro-2-(4-methoxyphenyl)-2H-1,3-benzoxazine	0	0	0	0	0	0,75	0	0	0	0	0	0	0
51.85	5-(4-Methoxybenzylideneamino)penta n-1-ol	4,074	0	0	0	0	0	0	0	0	0	0	0	0
53.34	7,11-Epoxy megastigma-5(6)-en-9-one	0	0	0	0	0	0	0	0	0	2,928	0	0	0

53.4 2	1-Butanamine, N-(3-phenyl-2-propenylidene)-	0	9,239	0	0	0	0	0	0	0	0	0	0	0
55.5 3	Benzyl Benzoate	0	7,836	0	0	0	0	0	0	0	0	0	0	0
56.2 7	Ethyl 14-hydroxy-3,6,9,12-tetraoxatetradecan-1-oate	0	0	0	0	0	0	0	0	0	0	0	1,852	0
58.6 1	Hinokitol	2,488	0	0	0	0	0	0	0	0	0	0	0	0

Starting from Table 1 listing all 204 VOCs identified in this study, most are compounds present in more than one oil. On the contrary, in Table 2, characteristic VOCs for each one of the samples are shown, sorted by decreasing abundance. After the analysis 95 compounds out of 204 were characteristic of one of the selected essential oils, this identified molecules could be used in future works as markers of the presence of a determinate essential oil. In terms of abundance the oils that present characteristics chemical compounds from higher to the lower number were ordered as: Cinnamon (15), Juniper (14), Nutmeg (12), Carnation (11), Mustard (9), Cardamom (8), Basil and Oregano (6 respectively), Niaouli and Thyme (4 respectively), Coriander (3), Rosemary (2) and Cayeput (1).

Table 2. Characteristic VOCs for each EO, sorted by decreasing abundance.

EO	Characteristic VOCs
Basil	Estragole
	N-[2-[p-Methoxybenzyl]amino]ethylaziridine
	[4.2.2]Propella-2,4,7,9-tetraene
	5-(4-Methoxybenzylideneamino)pentan-1-ol
	Hinokitol
	P-Anisaldehyde
Cinnamon	Isoledene
	Cinnamyl ester acetic acid
	N-[(4-Hydroxy)hydrocinnamoyl]-Benzeneethanamine
	Pseduosarsasapogenin-5,20-dien methyl ether
	Benzaldehyde
	Cinnamyl alcohol
	1-Chloroeicosane
	1-Butanamine, N-(3-phenyl-2-propenylidene)-
	Benzyl Benzoate
	Aromandendrene
	1-Chloro-Heptacosane
	5-Benzoylpentanoic acid
	α -Calacorene
	Acetocinnamone
	Tridecyl adamantane-1-carboxylate
Cardamom	Methyl Heptenone
	Limonene glycol
	3-Chloro-2-methyl-2-pentanol
	Pinocarveol
	(+)-(E)-Limonene oxide

	Methoxyethylene
	Dehydroterpin Monoacetate
	1,3,3-Trimethyl-6-hydroxy-2-oxabicyclo[222]octan-7-one
Cayeput	1-Heptadecene
Coriander	Ethyl 2-(5-methyl-5-vinyltetrahydrofuran-2-yl)propan-2-yl carbonate
	1-Tetradecene
	N,N-Dimethyl-3-Buten-1-amine
Carnation	2-Heptanol
	(2-Methyloctyl)benzene
	Methyl undecyl ether
	N-(2-Furanylmethylene)-3-methyl-1-butanamine
	Benzenepropanoic acid, β -[(tert-butyl)dimethylsilyloxy]-, tert-butyl)dimethylsilyl ester
	1-Octadecene
	1,2-Nonadecanediol
	1-Undecene
	trans-Octahydro-2-(4-methoxyphenyl)-2H-1,3-benzoxazine
	3-chlorophenyl 2-methoxyethyl ester carbonic acid
	p-Propylguaiaicol
	β -Curcumene
	Pentamethylcyclopentadiene
	α -Cadinol
	Longifolene-(V4)
	trans-calamenene
	1-Ethyl-2,3-dimethyl-piperidin-4-one
	Isopinocarveol
	Geranylinalool
	Geranyl- α -terpinene
	Manoyl oxide
	7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene
	Sclarene
	Longifolene-I2
	Hedycaryol
Niaouly	Myrcenol
	1-Undecanol
	Undecyl pentafluoropropionate
	α -Terpinyl acetate
Nutmeg	3-Isopropenyl-5,5-dimethyl-cyclopentene
	1,4-Dimethyl-4-vinylcyclohexene
	Asarone
	cis-p-Mentha-2,8-dien-1-ol
	cis-p-Menth-2-en-1-ol
	1-Adamantanol
	β -copaene
	cis-sesquisabinene hydrate
	trans-p-mentha-1(7),8-dien-2-ol
	Isomethyleugenol
	Guaiol
	Isosafrol
Oregano	β -Terpineol
	2-Octen-1-ol, 3,7-dimethyl-, isobutyrate, (Z)-
	N-[4-Bromo-n-butyl]-2-piperidinone

	Bicyclo[3.2.0]hept-2-ene, exo-4-tertbutoxy-
	7,11-Epoxy-megastigma-5(6)-en-9-one
	(2 α ,3 α ,5 β)-1,1,2-Trimethyl-3,5-bis(1-methylethenyl)-cyclohexane
Rosemary	p-Menth-2-en-1,4-diol
	Humulen-(v1)
Mustard	Diallyl sulfide
	Cyclopropylamine
	Thiazole
	1-(2,6-Dimethylmorpholin-4-yl)-2-ethyl-hexan-1-one
	3-Butyl-cyclopentanone
	1-Butoxy-2-ethylhexane
	Ethyl 14-hydroxy-3,6,9,12-tetraoxatetradecan-1-oate
	bis(dimethylhydrazone)ethanedial
	2-Methyl-2-(2,2,4,4-tetramethylpentyl)-aziridine
Thyme	2-(3,4-Dibromo-4-methylcyclohexyl)propan-2-ol
	1-(1-Methoxymethoxyethyl)cyclohexene
	1-Decylaziridine
	Dihydro carveol

Finally, Figure 1 shows a histogram of the frequency of most common VOCs. This 38 VOCs represent the ones that are present in at least seven of the oils. The class of compounds most represented is that of terpenes as widely reported in cited literature, with 10 monoterpenes (1R- α -pinene, (+)-4-carene, β -pinene, γ -terpinene, 4-carvomenthenol, M-cymene, L- α -terpineol, carvacrol, β -myrcene, camphene) and 1 sesquiterpene (caryophyllene); the other two are alcohols (1-octanal, 2-ethylhexanol, 2-methyldecan-1-ol, 1-[1-methyl-2(2-propenyloxy)ethoxy]-2-propanol, 1-dodecanol, 1-(isooctyloxy)-2-methyl-2-propanol, 4-methyl-3-heptanol, 1-methoxy-2-propanol) and ether (polypropylene glycol methyl ether, eucalyptol, dipropylene glycol monomethyl ether, ethylene glycol monododecyl ether, diethylene glycol hexyl ether, octyl ether, ethyl glycidyl ether, diethylene glycol monododecyl ether) with 8 compounds each.

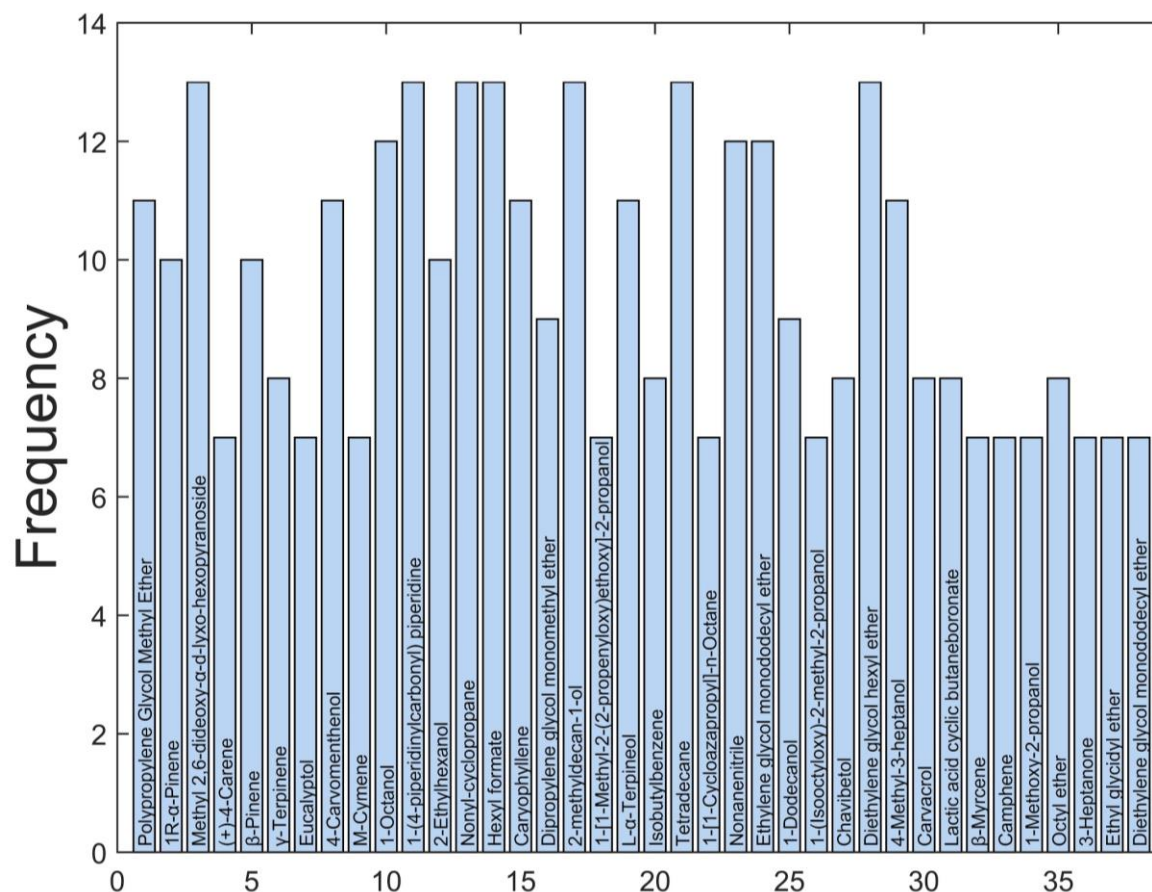


Figure 1. Frequency of the most common compounds among the 13 EOs. 38 are the compounds that appear in at least seven of the oils.

2.2. S3 Analysis

Analysis of the data collected with S3 has been carried out using Principal Component Analysis (PCA). In this PCA, features extracted from 7 out of 8 sensors were considered. Indeed, one RGTO SnO₂ (heated at 400°C) sensor has been discarded since there was no difference in responses to the different samples. The 2D biplot is shown in Figure 2; it has been done considering the first two principal components (PCs) for a total explained variance equal to 95,45% (78,27% for PC1, 17,18% for PC2). Loadings names are sensors morphology (NW stands for nanowire, RGTO for Rheotaxial Growth and Thermal Oxidation) followed by sensors material. The dotted line separates the two clusters that can be identified: in the upper half-plane juniper, nutmeg, rosemary and mustard samples are situated, the others are in the lower half-plane. The only exception is represented by one measure of coriander that is in the opposite part of the line compared to the others and it is most likely an outlier.

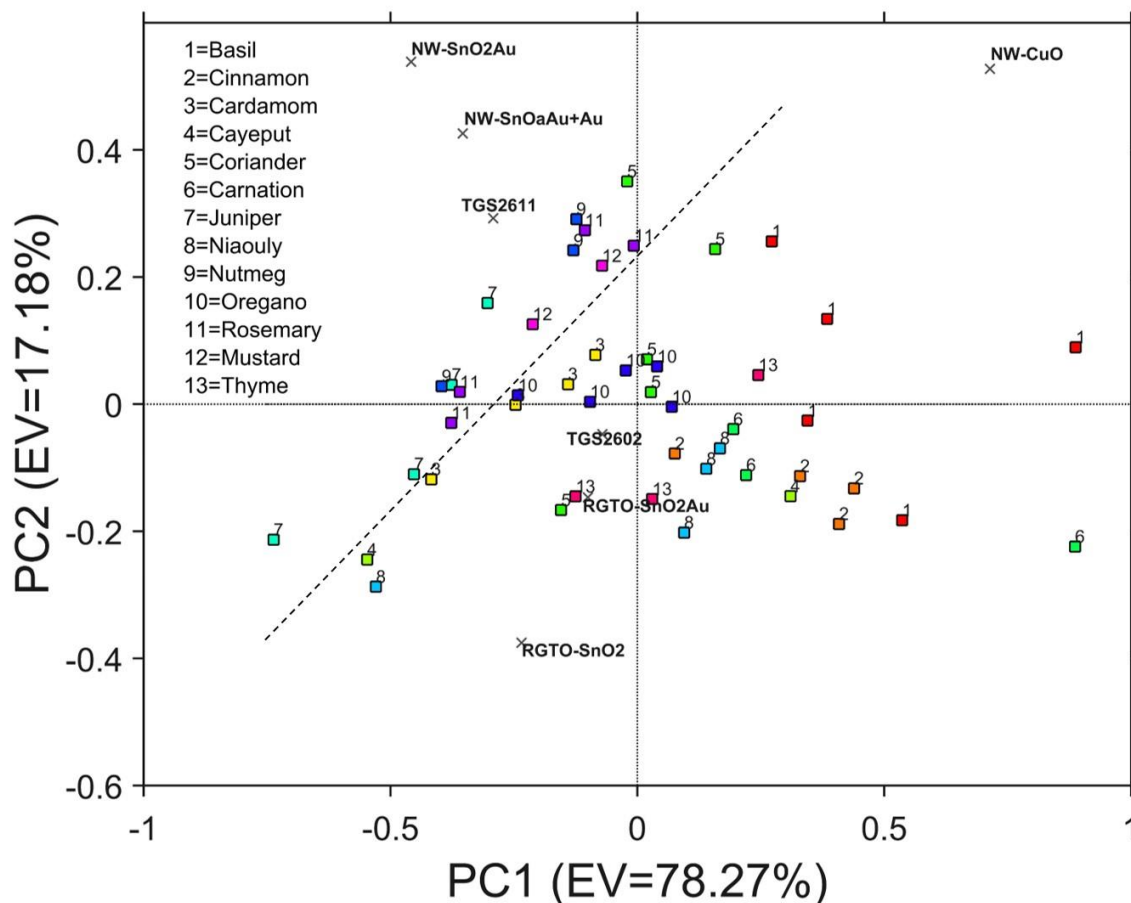


Figure 2. PCA of the first two principal components (total explained variance equal to 95.45%). Loadings are indicated with crosses, samples with squares and relative number. Legend is in the upper left part of the graph.

To understand which compounds were at the base of the division of the two clusters, Analysis of Variance (ANOVA) has been applied. 7 VOCs had means significantly different between the two groups: five of them were characteristic compounds of specific EOs (cyclopropylamine and diallyl sulfide for mustard, 2-Methyloctylbenzene for carnation, 1-Decylaziridine for thyme, N-[2-[p-Methoxybenzyl]amino]ethylaziridine for basil), one was common for three EOs (8-Methylenepentadecane in cayecout, niaouly and rosemary) and one was found in all the samples (Tetradecane).

Furthermore, an explanation was sought for the fact that there is no clear separation between the different oils. Looking at the common compounds of Figure 1, seven VOCs were found in all the samples. They are methyl 2,6-dideoxy- α -d-lyxo-hexopyranoside; 1-(4-piperidinylcarbonyl) piperidine; nonyl-cyclopropane; hexyl formate; 2-methyldecan-1-ol; tetradecane; diethylene glycol hexyl ether. The relative amount of these VOCs compared to the total ranges from 11.7% to 36.8%. Samples in the upper half-plane of the Figure 2 are characterized by low percentages (from 11.7% to 14.19%), except for mustard (36.8%). However, the fact that mustard is in the same area could be due to its characteristic VOCs. Indeed, they contain different atoms respect to the other EOs, that are nitrogen and sulfur. Samples in the lower half-plane have a higher content of these seven compounds, from 16.2% to 35.5%. In that case, the EO with the bigger percentage is carnation; however, since an alcohol (2-heptanol) is its most abundant characteristic compound, carnation samples are in the opposite half-plane respect to mustard ones despite the similar amount of compounds in common.

Finally, capability of sensors to distinguish one or more EOs from the others were identified with ANOVA. Hence, the number of times a specific couple of EOs showed significant different means, *i.e.* recognition by the sensor, has been added. The results are reported in the heatmap below

(Figure 3), where 0 means that none of the sensors is able to achieve the discrimination and 7 that all of them are capable to do a distinction. All the sensors of the array succeed to identify basil from juniper and six of them basil from cardamom (the only exception is TGS2611). Three nanowire sensors (CuO, SnO₂Au+Au and SnO₂Au) and both TGS showed the ability to distinguish juniper from cinnamon and carnation. Both tin oxide nanowire and TGS sensors allow the recognition of nutmeg from basil and carnation, of rosemary from basil, cinnamon and carnation, of mustard from basil. Less recognizable EOs are thyme and cayeput (separated only from basil), followed by cardamom and coriander (distinguished from basil, cinnamon and carnation). Conversely, basil, cinnamon and carnation are the most identified oils.

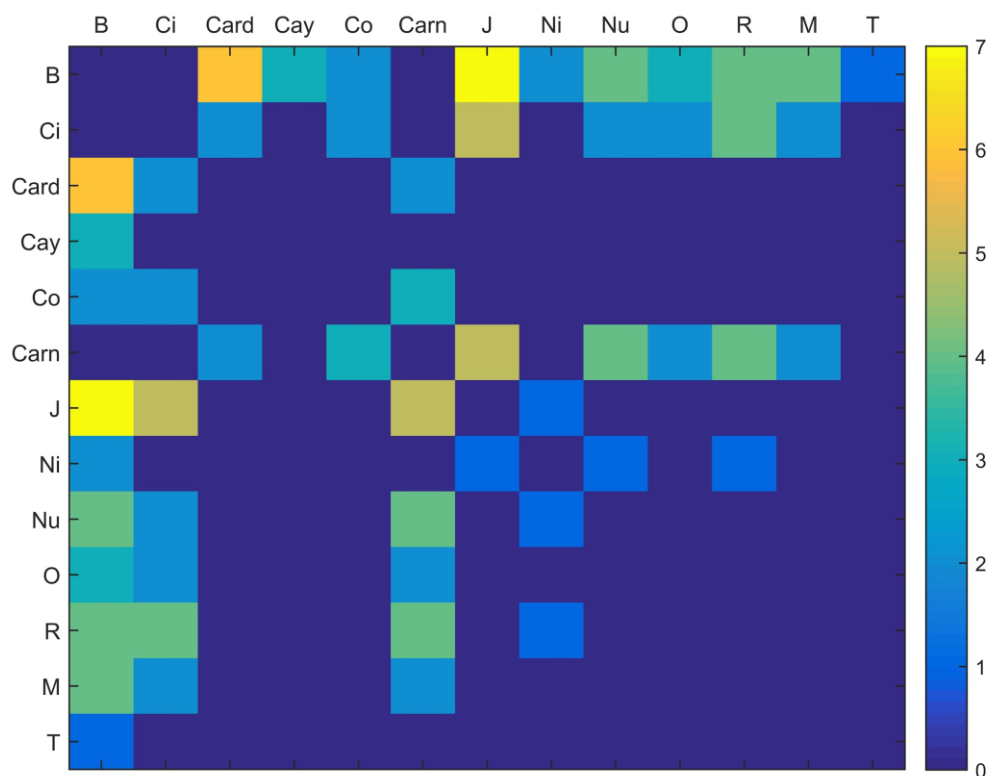


Figure 3. Heatmap regarding the number of sensors useful to discriminate between couples of EOs. B=basil, Ci=cinnamon, Card=cardamom, Cay=cayeput, Co=coriander, Carn=carnation, J=Juniper, Ni=niaouly, Nu=nutmeg, O=oregano, R=rosemary, M=mustard, T=thyme.

This preliminary study shows that chemical sensors have potentials to be used to recognize some EOs. In future works, the parameters of analysis could be adjusted to improve the ability of the system to identify more oils. In particular, new methods that allow to highlight the different VOCs and to reduce the influence of common compounds should be put in place.

3. Materials and Methods

3.1. Samples

Thirteen EOs were considered: basil, cinnamon, cardamom, cayeput, coriander, carnation, juniper, niaouly, nutmeg, oregano, rosemary, mustard, thyme. Of the thirteen EOs, three of them came from Sigma-Aldrich (Saint Louis, Missouri, USA) and are cardamom, oregano and mustard; the others were bought at Solimè S.r.l. company (Reggio Emilia, Italy).

Analyzed samples were stored at room temperature, far from sources of heat and light. From each of the thirteen EOs, 37.5 μ l were taken and put in 20 ml glass vials containing 5 ml of distilled water. The main reason for choosing this concentration was to avoid the saturation of sensor response, due to the high interaction between the amount of VOCs and the sensing material. Hence, the vials were sealed with a metal cap with a PTFE-silicon membrane crimped with an aluminum crimp. For both types of sample, prepared for the measurements with GC-MS and with S3, a method was developed that envisaged optimizing the equilibrium of liquid phase and vapor phase inside the crimped vial, therefore waiting 1 hour before proceeding to the analysis. Two specimens were prepared for GC-MS, while a different number of replicas has been prepared for S3, for a total of 48 measures. The detailed number of samples for each EO is reported in the Table 3.

Table 3. Detailed number of samples for each kind of EOs respectively for each technique used.

N°	EOs Name	GC-MS N° of Samples	S3 N° of Samples
1	Basil	2	5
2	Cinnamon	2	4
3	Cardamom	2	4
4	Cayeput	2	2
5	Coriander	2	5
6	Carnation	2	3
7	Juniper	2	4
8	Niaouly	2	4
9	Nutmeg	2	3
10	Oregano	2	5
11	Rosemary	2	4
12	Mustard	2	2
13	Thyme	2	3
Total		26	48

3.2. GC-MS Analysis

The Gas Chromatograph (GC) used during the analyses was a Shimadzu GC2010 PLUS (Kyoto, KYT, Japan), equipped with a Shimadzu single quadrupole Mass Spectrometer (MS) MS-QP2010 Ultra (Kyoto, KYT, Japan) and an autosampler HT280T (HTA s.r.l., Brescia, Italy). The GC-MS analysis was coupled with the Solid-Phase Micro Extraction (SPME) method in order to find the most characteristic VOCs for each sample.

The fiber used for the adsorption of volatiles was a DVB/CAR/PDMS-50/30 μ m (Supelco Co. Bellefonte, PA, USA). The fiber was exposed to the headspace of the vials after heating and shaking

the samples in the HT280T oven, thermostatically regulated at 50 °C for 15 min, with the aim of creating the headspace equilibrium. The length of the fiber in the headspace was kept constant. Desorption of volatiles took place in the injector of the GC-MS for 6 min at 250 °C.

The gas chromatograph was operated in the direct mode throughout the run, with the mass spectrometer in electron ionization (EI) mode (70 eV). GC separation was performed on a MEGA-WAX capillary column (30 m × 0.25 mm × 0.25 μm, Agilent Technologies, Santa Clara, CA, USA). Ultrapure helium (99.99%) was used as the carrier gas, at the constant flow rate of 1.3 mL/min. The following GC oven temperature programming was applied. At the beginning, the column was held at 40 °C for 8 min, and then raised from 40 to 190 °C at 4 °C/min; then, the temperature was maintained at 190 °C for 5 min. Next, the temperature was raised from 190 °C to 210 °C, with a rate of 5 °C/min; finally, 210 °C was maintained for 5 min.

The GC-MS interface was kept at 200 °C. The mass spectra were collected over the range of 45 to 500 *m/z* in the Total Ion Current (TIC) mode, with scan intervals at 0.3 s. The identification of the volatile compounds was carried out using the NIST11 and the FFNSC2 libraries of mass spectra.

3.3. S3 Analysis

S3 device used in the present work has been completely designed and constructed at SENSOR Laboratory (University of Brescia, Italy) in collaboration with NASYS S.r.l., a spin-off of the University of Brescia. It has been described in other works [39,40-45,46]. Briefly, the tool comprises three parts: pneumatic components, that transfer VOCs from the head-space of samples to the sensing chamber; electronic boards, that manage the acquisition and transmission of the data from the device to the dedicated Web-App and allow the synchronization between S3 and the auto-sampler; sensing chamber, that can host from five to ten different MOX gas sensors and is thermostated and isolated in order to avoid any influence of the surrounding environment. To function properly, the sensors need a reference value, which has been obtained by filtering the ambient air with a small metal cylinder (21.5 cm in length, 5 cm in diameter) filled with activated carbons.

Eight MOX gas sensors were used. Three of them are MOX nanowire, as presented in References [34]. Two of them are tin oxides nanowires sensors, both grown by means of the Vapor Liquid Solid technique [47], using a gold catalyst on the alumina substrate and functionalizing one of them with gold clusters; the third sensor has an active layer of copper oxide nanowires. The working temperature is 350 °C, 350 °C and 400 °C, respectively. The other three sensors are prepared with RGTO thin film technology [48]; one is tin oxide functionalized with gold clusters (working at 400 °C), while the other two are pure tin oxide (working at 300 °C and at 400 °C, respectively). The last two are commercial MOX sensors produced by Figaro Engineering Inc. (Osaka, Japan). In particular, they are the TGS2611 and TGS2602, which are sensitive to natural gases and odorous gases like ammonia, respectively, according to the datasheet of the company. Commercial sensors have been mounted on our e-nose in order to evaluate the performances of nanowire sensors. Details of S3 sensors made at SENSOR Laboratory are summarized in Table 4. Response to 5 ppm of ethanol, selectivity (response ethanol/response carbon monoxide) and limit of detection (LOD) of ethanol are also included.

Table 4. Type, composition, morphology, operating temperature, response ($\Delta R/R$), selectivity (response ethanol/response carbon monoxide) and limit of detection (LOD) of ethanol for S3 sensors made at the SENSOR Laboratory.

Materials (Type)	Composition	Morphology	Operating Temperature (°C)	Response to 5 ppm of Ethanol	Selectivity	Limit of Detection (LOD) of Ethanol (ppm)
SnO ₂ Au (n)	SnO ₂ functionalized with Au clusters	RGTO	400 °C	6.5	3	0.5
SnO ₂ (n)	SnO ₂	RGTO	300 °C	3.5	2.5	1
SnO ₂ (n)	SnO ₂	RGTO	400 °C	4	2	0.8
SnO ₂ Au+Au (n)	SnO ₂ grown with Au and functionalized with gold clusters	Nanowire	350 °C	7	2.5	0.5
SnO ₂ Au (n)	SnO ₂ grown with Au	Nanowire	350 °C	5	2.1	1
CuO (p)	CuO	Nanowire	400 °C	1.5	1.5	1

The auto-sampler head-space system HT2010H was coupled with S3. It supports a 42-loading-sites carousel and a shaking oven to equilibrate the sample head-space. The vials were placed in a randomized mode into the carousel. Each vial was incubated at 40 °C for 5 min in the auto-sampler oven and shaken every 6 s for 12 s during the incubation. The sample head-space was then extracted from the vial in the dynamic head-space path and released into the carried flow (50 sccm). The analysis timeline can be divided into three different steps for a duration of 600 s (10 min) per sample, 60 s to analyze samples and 510 s to restore the base line. Thanks to the processor integrated in the S3 instrument, the frequency at which the equipment works is equal to 1 Hz.

3.4. Data Analysis

Statistical techniques have been applied to extract information from S3 data. PCA has been performed to understand if the array of sensors was able to discriminate among the EOs. Hence, $\Delta R/R$ feature has been calculated for the eight sensors as input variables. Sequentially, ANOVA has been used to interpret grouping of the EOs on the 2D biplot and to individuate best sensors for EOs discrimination, selecting a significance level equal to 0.05. Finally, multiple comparison of the ANOVA results has been done using Tukey's honest significance test.

4. Conclusions

Thanks to this detailed study, it has been possible to reach and obtain different important points for the future development of this type of research. Especially as regards the results obtained with the GC-MS, it has been highlighted that 95 out of 204 VOCs characterize one oil from the others. As far as S3 is concerned, the results obtained and the conclusions that we can draw from it can be further divided into two parts, a part concerning the whole array and a part related to the responses of the individual sensors to the analyzed oils. Through PCA, it can be suggested that S3 was able to distinguish between two clusters: one is formed by juniper, nutmeg, rosemary and mustard, the other by basil, cinnamon, cardamom, cayeput, coriander, carnation, niaouly, oregano and thyme. From the analysis of individual sensors, it turned out that basil, cinnamon and carnation are the most identifiable oils with different number and typology of sensors, especially tin oxide and copper oxide nanowires, while cayeput and thyme are more mistakable samples.

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